

SPATIAL AND TEMPORAL PATTERNS OF INORGANIC NITROGEN AND PHOSPHORUS  
DISTRIBUTIONS IN THE GOOSE CREEK ESTUARY: COOPER RIVER/CHARLESTON HARBOR  
ESTUARY SYSTEM

by

Adriene Purette Douglas  
Bachelor of Science  
Indiana University of Pennsylvania, 1986

Submitted for Partial Fulfillment of the  
Requirements for the Degree of Master of Science in Public Health  
in the Department of Environmental Health Sciences  
School of Public Health

University of South Carolina  
1995

## ABSTRACT

The control of estuarine water quality and eutrophication requires a detailed understanding of the spatial and temporal distributions of the major limiting nutrients. The main objective of this study was to quantify dominant patterns of nutrient distributions in the Goose Creek sub-basin of the Cooper River estuary, a major urbanized estuary in South Carolina. This sub-basin enters the mesohaline reaches of the Cooper River estuary and extends upstream to a tidal freshwater marsh region. Inorganic nutrients, ammonium, nitrate, and orthophosphate were examined along the salinity gradient of the Goose Creek estuary on a monthly basis in relation to tidal stage, tributary inputs and point source wastewater discharges from June 1992 to November 1993.

Orthophosphate concentrations varied from 0.3 to 5.3  $\mu\text{g-at/l}$  with an overall mean of  $1.3 \pm 0.1 \mu\text{g-at/l}$ . Significant regional differences emerged only during the summer when concentrations near the mouth (lower estuary) were 26 to 39 % higher than in the upper oligohaline region of the estuary, indicating a major influence of the Cooper River on the orthophosphate distribution in Goose Creek. Although municipal wastewater discharges of orthophosphate to the upper estuary caused local elevated concentrations in the estuary, this effect was not evident in regional differences. The overall mean concentration in municipal wastewater discharge ( $160 \pm 63 \mu\text{g-at/l}$ ) was significantly higher than that in waters from urban tidal ( $1.6 \pm 0.3$  to  $1.8 \pm 1.0 \mu\text{g-at/l}$ ) and forested ( $1.7 \pm 0.4$  to  $1.8 \pm 1.0 \mu\text{g-at/l}$ ) tributaries.

Ammonium ranged from 1 to 138  $\mu\text{g-at/l}$  with a mean of  $9.7 \pm 1.0 \mu\text{g-at/l}$  for the study period. Elevated ammonium concentrations during the summer may have been caused by interacting point source wastewater discharges, tributary inputs and remineralization. The overall mean concentration in municipal wastewater discharge ( $202.2 \pm 66 \mu\text{g-at/l}$ ) was significantly higher than in waters from urban tidal ( $18.5 \pm 2.4$  to  $18.8 \pm 3.8 \mu\text{g-at/l}$ ) and forested ( $6.5 \pm 2.6$  to  $11.8 \pm 5.6 \mu\text{g-at/l}$ ) tributaries.

Nitrate concentrations ranged from 1 to 49.5  $\mu\text{g-at/l}$  with a mean of  $11.9 \pm 0.5 \mu\text{g-at/l}$  for the study period. Nitrate displayed a distinct seasonal pattern and concentrations in the fall ( $14.0 \pm 0.9 \mu\text{g-at/l}$ ) were significantly higher than in the winter ( $8.5 \pm 0.8 \mu\text{g-at/l}$ ). Remineralization, nitrification, and municipal point source input contributed to the elevated concentrations during the summer. Significant regional differences occurred during the summer, with concentrations being higher in the upper ( $14.3 \pm 1.3 \mu\text{g-at/l}$ ) estuary than in the lower ( $8.6 \pm 1.0 \mu\text{g-at/l}$ ) estuary. Municipal wastewater discharges contributed to elevated nitrate concentrations in the upper estuary, and this peak was displaced downstream resulting in significantly higher concentrations in the middle region than the lower region of the estuary. The overall mean nitrate concentration in municipal wastewater discharge ( $569.7 \pm 110 \mu\text{g-at/l}$ ) were significantly higher than in waters from urban tidal ( $15.2 \pm 2.1$  -  $25.6 \pm 3.5 \mu\text{g-at/l}$ ) and forested ( $1.0 \pm 0.4$  to  $2.9 \pm 0.9 \mu\text{g-at/l}$ ) tributaries. Nitrate concentrations in urban tributaries were significantly higher than in forested tributaries.

## INTRODUCTION

Eutrophication or over-enrichment of inorganic nutrients is a serious problem in urbanized estuaries and coastal waters. Increased nutrients in coastal waters can cause an increase in phytoplankton production (Ryther and Dunstan 1971; Jaworski et al. 1992; Valiela et al. 1992), depletion of dissolved oxygen (Valiela et al. 1992) and changes in the species composition. Water quality impairments observed in an estimated 55 % estuaries were traced to elevated nutrient concentrations (Davenport 1994). In coastal urbanized watersheds municipal and industrial wastewaters and stormwater runoff are major sources of nutrients in estuarine ecosystems. A combination biochemical transformations occurring in the water column and sediments and freshwater input from surface waters (e.g. rivers, streams, ponds) influence the distribution of nutrients. The assessment of nutrient distribution in an urbanized estuary will provide a nutrient data to supplement other types of information (hydrology and land use) to aid both coastal developers and estuarine managers in making the best decisions on how to manage estuarine water quality.

In estuarine water, nitrogen and phosphorus exists in the dissolved and particulate form. Dissolved phosphorus is composed of the organic and soluble reactive (orthophosphate) forms. Orthophosphate is utilized by aquatic plants. The particulate forms of phosphorus include inorganic and organic phosphorus adsorbed to sediment, detritus, and bacteria. For nitrogen, the forms exist as organic, ammonia, nitrite plus nitrate. The organic components of nitrogen are in a dissolved state and associated with detrital particles. Ammonia and nitrite plus nitrate are in an inorganic state and available for plant uptake. McCarty (1977) observed that phytoplankton prefer the uptake of ammonium over nitrate in most cases.

Nutrients generated by urban activities such as residential, commercial and industrial activities enter the estuary through two principal inputs: point source and nonpoint source discharge. Point source discharge is direct and identifiable and includes a more traditional source: municipal and/or industrial wastewater. This type of discharge is typically continuous and not affected by meteorological factors. Nonpoint source discharge, on the otherhand, is indirect and diffuse. In addition, nonpoint source discharge is transient and precipitation dependent, so significant amounts of nutrients are flushed in the estuary via surface runoff during heavy rains.

Wastewater from secondary biological treatment plants, which employ the activated sludge process, contains large amounts of ammonium and nitrate. Organic matter discharged with wastewater to the estuary can undergo microbial decomposition and potentially contribute significant amounts of inorganic nitrogen. Industrial discharges are also sources of inorganic and organic wastes.

Urban watersheds characteristically have significant amounts of impervious surfaces. These surfaces exhibit virtually no infiltration, are hydrologically active and can potentially yield appreciable stormwater runoff in response to significant rainfall. Nutrient sources carried in rain-generated surface runoff include domestic wastes, plant litter, and sediment, as well as other sources, and thus contributes to urban nonpoint source pollution.

Non-urbanized forested areas are generally recognized as insignificant sources of nutrients (Corbett et al. 1978 and Martin et al. 1984). A number of studies have shown that streamside forests of coastal plain watersheds can effectively reduce the flux of nutrients to streams and rivers (Sweeney 1992). Climate, soil morphology, vegetation and topography may be responsible for the release of low quantities to streamwater from these ecosystems. Both the vegetative canopy and soil of a forested ecosystem serves as a buffer to protect the water chemistry of receiving waters by removing excessive nutrients.

When natural areas are put to agricultural use, nutrient and sediments in streams draining these areas increases (Hopkins and Clausen 1985). In the coastal plains, agricultural lands are often major sources of nutrient discharge and release more nutrients than do forested uplands (Correll et al. 1992).

In estuaries the distribution of dissolved inorganic nitrogen is typically controlled by biological and chemical processes found in the water column and/or sediments when input of freshwater is low or varies throughout the year. These constituents either settle out or become

regenerated within the system. Sources of dissolved inorganic phosphorus include iron and manganese phosphate complexes released from the sediments under anaerobic conditions. Once sediments are reduced the soluble form of these complexes is produced and releases orthophosphate to the overlying water. Remineralization of organic phosphorus on the sediments also releases orthophosphate to the water. Temperature has been suggested as the most influential factor controlling this process. The seasonal pattern for sediment regeneration of orthophosphate for different estuarine systems ranging from a river dominated system to a lagoon was similar, with a mid-summer peak (Day et al. 1989). Other processes can contribute orthophosphate to the estuary such as planktonic excretion in the water column and charged clay particles in sediments (Day et al. 1989).

Sediments have been hypothesized as being sinks for orthophosphate for a few estuaries (Boynton and Kemp 1985; Teague et al. 1988). Low orthophosphate release from sediments has been observed in the Potomac River estuary and the Fourleague Bay and attributed to the high sorption capability of silt and clay in the sediments. In addition, an oxygenated water column facilitates the binding of orthophosphate with iron ( $\text{Fe}^{+3}$ ) and results in the sedimentation of this complex, thereby preventing the diffusion of orthophosphate to the overlying water column.

Phytoplankton uptake in the water of the Chesapeake and Delaware Bays was recognized as an important removal mechanism for orthophosphate (Fisher et al. 1988). The orthophosphate minimum in both estuaries occurred when the maximum amount of chlorophyll a was detected. Flocculation, the coalescing of particles into large aggregates, serves as a temporary removal mechanism for orthophosphate. This process can effectively remove this nutrient from regions within the estuary having a high content of suspended materials (silts and clays) and salinities between 0 and 5 ppt (Day et al. 1989).

The inorganic pool for nitrogen is more diverse than that of phosphorus. It is composed of three different chemical constituents: ammonium, nitrite, and nitrate. In aerobic environments, nitrite is generally oxidized quickly to nitrate and is considered to have the least effect on the nitrogen cycle in the estuarine environment. In shallow estuaries biological processes can dominate the distribution of nutrients. Nitrate can be produced in the water column by nitrification. Nitrification is the bacterial oxidation of ammonium to nitrate under aerobic conditions. The most important environmental factors that influence nitrification are temperature (Berounsky and Nixon 1993), oxygen (Boynton and Kemp et al. 1985), and ammonium (Berounsky and Nixon 1993). This process follows the annual temperature cycle with the highest rates occurring in the summer at a time when microbial respiration is greatest. Summer nitrification rates in the Narragansett Bay vary spatially depending on the abundance of ammonium (Berounsky and Nixon 1993); higher nitrification rates were seen in regions with relatively high ammonium concentrations presumably near point sources.

In the estuarine environment nitrate can be depleted by denitrification. Denitrification is the bacterial-mediated reduction of nitrate to gaseous nitrogen ( $\text{N}_2$ ,  $\text{N}_2\text{O}$ ) in anaerobic sediments concomitant with the oxidation of organic matter. Phytoplankton can affect the seasonal pattern of denitrification. High nitrate uptake by phytoplankton during the spring and summer lowered denitrification rates in some estuarine sediments (Delaware Bay - Pennock 1987; Norsminde Fjord - Koike and Sorensen 1988). Elevated denitrification rates have been found in marsh sediments where the supplies of organic substrate (Koike and Sorenson 1988) and nitrate (Nisho 1982; Koike and Sorenson 1988) are high. Seitzinger (1982) measured denitrification in the sediments of microcosms treated with various levels of nitrate and found that a ten fold increase in nitrate loading corresponded to a five-fold increase in the rate of denitrification. Thus, field and laboratory data indicates that denitrification is limited by nitrate availability.

Since sediments are often a major sink for nitrogen in estuaries and these systems are regarded as being nitrogen limited, sediment remineralization (regeneration) can play an important role in the recycling of nitrogen in the estuary. Nitrogen resulting from the microbial decomposition of organic matter is released from oxidized sediments in the form of ammonium. Organic matter is generally mineralized in the upper few centimeters of sediments. Ammonium regeneration from the sediments varies with temperature and is most pronounced during the summer (Kemp et al. 1990). Boynton and Kemp (1985) suggest that sediments are a significant source of ammonium for

plankton. In the mid-salinity (12 to 17 ppt) region of the Chesapeake Bay 13 to 40 % of the phytoplankton demand was supplied by the sediment regeneration of ammonium (Boynton and Kemp 1985). Recycled ammonium may undergo transformations within the sediments that are unrelated to temperature and become unavailable for phytoplankton uptake. In aerobic sediments, ammonium released in decomposition may be nitrified into nitrate and subsequently diffuse to the overlying waters.

Freshwater discharge to the estuary can dominate nutrient distributions. During wet periods, particularly in the winter and spring, large freshwater flows cause the distributions to be linear with respect to salinity (Peterson 1985). Nutrients within the estuary are subjected to biochemical processes under low flow conditions during the summer (Peterson 1985).

The Goose Creek estuary is a brackish sub-basin of the Cooper River/Charleston Harbor Estuary system. With a representative mix of landuses such as urban and forested and point source and nonpoint source input discharges, physical characteristics and distributions of nutrients could change. A reservoir at the head of the estuary provides the dominant source of freshwater to maintain adequate estuarine flow. The main objectives in this study were 1) to quantify the dominant spatial and temporal patterns of temperature, salinity, dissolved oxygen, and nutrients (nitrogen and phosphorus) and 2) to evaluate the relative importance of nonpoint source inputs from urban and forested watersheds and point source inputs from municipal and industrial discharges on nutrient distributions. These examinations were conducted in the context of seasonal changes in rainfall, freshwater flow and estuarine ecosystem functioning.

## Study Site

Goose Creek is a subtributary estuary of the Cooper River estuary and located approximately 22 km upstream from the Charleston Harbor, on the South Carolina coast, USA (Fig. 1). The estuary extends from the Goose Creek Reservoir 15.60 km downstream to the mesohaline reaches of the Cooper River (Fig. 1). In accordance with its SC water quality classification, no harvesting of shellfish (i.e. clams, oysters, and mussels) is permitted and dissolved oxygen shall not go below 4 mg/l at any time.

The 4000 ha watershed surrounding the Goose Creek estuary is a mixture primarily of urban and forested land. Currently, 33 % of the land is upland pine hardwood forest and 39 % is urban and located on the north and south side of the estuary, respectively. Urban land is used for residential (single units), commercial, transportation and industrial uses. Nineteen percent of the basin is nonforested wetland and lies contiguous with the estuarine reach of Goose Creek. The lower 13 km of the estuary has wetlands dominated mainly by *Spartina alterniflora* with patches of *Juncus roemarianus*. The upper 3 km of the estuary is a tidal freshwater environment where the wetlands are dominated by a more diverse set of plant species including *Typha*, *Zizaniopsis*, *Pontederia*, and *Peltandra*. Less than 2 % of the land is agricultural.

The Goose Creek reservoir (15.60 km upstream from the mouth) constitutes the head of the estuary and is the primary source of freshwater input to the estuary. The reservoir receives drainage from a 9300 ha watershed and additional input as inter-basin transfer from Foster Creek. During 1993, the reservoir accounted for more than 90 percent of the total freshwater entering the estuary (see Freshwater flow section). The eleven month mean discharge for the reservoir was 43.5 cfs (Rao, personal communication),

The main tributaries to the Goose Creek estuary include: Turkey Creek, Hanahan Creek, New Tenant Pond and Brown Pond. The outflows of two freshwater ponds, New Tenant Pond and Brown Pond, are located 5.76 and 4.80 km upstream from the mouth, respectively. Both ponds drain primarily forested land. Turkey Creek and Hanahan Creek are tidal creeks which are located on the south side of the estuary, 14.40 and 12.36 km from the mouth, respectively. These tributaries receive drainage largely from residential and commercial areas of towns; North Charleston and Hanahan.

Point source input to the estuary occurs in the upper region of the Goose Creek estuary. The Hanahan Wastewater Treatment plant and the Charleston County Public Waterworks facility, two point source input, are both located on the south bank of the estuary. The Hanahan Wastewater Treatment plant is located 12.24 km upstream from the mouth. This municipal plant employs the activated sludge process for treating domestic sewage waste and stormwater runoff coming from residential and commercial areas. The 1993 eleven month mean discharge for the treatment plant was 2.1 cfs. The Charleston County Public Waterworks facility is located 16.32 km upstream from the mouth and processes drinking water and discharges filter backwash as settling pond outflow into the Goose Creek estuary. The 1993 eleven month mean discharge to the estuary from Charleston County Public Waterworks facility was 2.3 cfs.

## Methods

### Sampling Design

Monthly sampling trips were scheduled from June 1992 through November 1993. The day of sampling was typically scheduled at times during the month near a neap tide to minimize the effects of extreme tidal flushing on nutrient distributions in the Goose Creek estuary. One month prior to and within this study, surface and bottom water samples were collected near the mouth of Goose Creek estuary and analyzed to determine depth variability of nutrient concentrations. A preliminary examination of the results showed a variability of  $< 1\%$  in nutrient concentrations between surface and bottom. Depth integrated water samples were collected along an eight station sampling transect in the estuary at high and low tide, (typically, within .5 hr of the predicted slack tide) to examine the existing tidal variability of nutrient concentrations. The estuarine stations (Fig. 1) were station 0 (zero km) at the mouth, station 1 (1.20 km), station 2 (3.84 km), station 3 (6.00 km), station 4 (8.64 km), station 5 (11.52 km), station 5b (12.24 km) at the sewage outfall, and station 6 (14.52 km). In addition to the routine sampling, duplicate water samples were periodically collected at 20 % of the estuarine stations to examine the field variability of nutrient concentrations.

The relative influence of urban and forested watersheds on nitrogen and phosphorus distributions in the Goose Creek estuary over time was evaluated by measuring the nutrient concentrations in waters from nonpoint and point sources. The only point source of urban-derived nutrients to the estuary was municipal wastewater. Nonpoint source discharges included those entering the estuary from the reservoir and tributaries receiving runoff from urban and forested land. Water samples were collected from sites representing different land use types at low tide usually one day prior to each mainstem sampling. Flow data for the reservoir were evaluated to relate changes in nutrient and water quality as a function of freshwater discharge.

All water samples were poured into acid-washed polyethylene bottles then placed on ice and transported to the laboratory within 24 hrs. of collection. Contemporaneously with each station sampled, physical parameters including dissolved oxygen, temperature, salinity were determined. Water temperature and DO were measured with the YSI - 55 DO meter and salinity with the YSI - TCS meter. During the latter part of the study, a YSI 3800 Water Quality Logger meter was used to measure all of these physical parameters.

On February 2 1994, water samples were collected at the eight monitoring stations along the estuary at both tides and analyzed for total nitrogen and total dissolved (soluble) nitrogen. Dissolved organic nitrogen was determined by the difference between total dissolved nitrogen and inorganic nitrogen (ammonium plus nitrate). Particulate nitrogen was determined by the difference between total and total dissolved nitrogen (inorganic and organic). Concentrations of nitrate and ammonium were also measured.

Although a thorough analysis of stormwater runoff from all sites was beyond the scope of this study period, an intensive sampling protocol was conducted at South Turkey Creek (a tributary of Turkey Creek and above the tidal influence) during the summer 1993 in order to examine one storm runoff event from an urban drainage area. The stream water was sampled and stream flow was measured twice daily (morning and afternoon) for 7 consecutive days from 27 July through 3 August. On 3 August, a thunderstorm occurred between 19:30 and 20:30 hrs. producing 0.39 inches of rain in about 1 hour. After the storm, the stream was sampled at peak flow (20:51 hrs.) and twice more during the falling limb of the hydrograph (21:20 hrs. and 22:50 hrs.).

### Sample Processing and Analysis

Nutrient analyses were generally conducted in a laboratory at the University of South Carolina, but for sampling dates July 1993, August 1993, and September 1993 analyses were conducted at the Baruch Institute Marine Field Laboratory in Georgetown, South Carolina. Samples for the determination of the dissolved inorganic nutrients nitrate + nitrite ( $\text{NO}_x$ ), ammonium ( $\text{NH}_4^+$ ), and orthophosphate ( $\text{PO}_4^{3-}$ ) were filtered through rinsed 0.45  $\mu\text{m}$  glass microfiber Whatman GF/F filters. The filtrate was then poured into 20 ml polyethylene scintillation vials. Since nitrite is typically the minor fraction of oxidized nitrogen, nitrate-nitrite will be referred to as nitrate. According to Degobbis (1973) samples for ammonium were preserved with .1 % (w/v) phenol and for

nitrate with 2 % (w/v) mercuric chloride. These samples were refrigerated at 4 °C up to 2 weeks before analysis. Orthophosphate was analyzed within 48 hrs. of sample collection; therefore, samples were not preserved. Ammonium concentrations were determined by the phenol hypochlorite method (Solarzano 1969), nitrate by the cadmium reduction method (APHA 1985), and orthophosphate by the acid molybdate method (Murphy and Riley 1962) using the Orion Scientific Segmented Flow Autoanalyzer. Dissolved organic nitrogen and total nitrogen were determined on filtered and unfiltered samples, respectively, using a spectrophotometric technique based on the alkaline persulfate digestion technique (Johnes and Heathwaite 1992). Applicable detection ranges for the methods mentioned above are 0 to 10 µg-at/l for ammonium, 0.1 to 5.0 µg-at/l for nitrate, and 0.0 to 5.0 µg-at/l for orthophosphate (APHA 1985). All nutrients were recorded as µg-at/L (microgram atom per liter). The mean of the differences in concentration between duplicate samples were  $0.3 \pm 0.1$  µg-at/l for orthophosphate,  $1.3 \pm 0.3$  µg-at/l for ammonium, and  $0.7 \pm 0.2$  µg-at/l for nitrate.

#### Data Analysis

Salinity measured at each of the eight sampling stations in the main channel over the 15 month study period were used to classify three broad regions in the estuary. Stations 0, 1, and 2 were grouped for the lower region, which were most influenced by the Cooper River. Stations 3 and 4 were grouped as the middle region. And stations 5, 5b, and 6 were grouped for the upper region with the greatest influence from the Goose Creek reservoir. In addition, high and low tide physical and nutrient data for each month were grouped according to season (fall, winter, spring, and summer). The seasonal units for this study were as follows: fall (September, October, and November), winter (January and February), spring (April and May), and summer (June, July, and August). Sampling did not occur during December 1992 or March 1993. For winter and spring, each month was represented by 1 sampling trip at high and low tides. Summer and fall data for 1992 and 1993 were combined yielding a total of 2 sampling dates for June, July, and August and 3 dates for October. A 15 month mean and seasonal average for each nutrient constituent was calculated for the headwater (reservoir), each non-point source discharge, and point source discharge stations.

Statistical analysis of nutrient and physical data was performed using the SAS software package (SAS 1985). Before performing certain statistical tests, a histogram inspection of the data from the 15 month sampling period was done to check for normality. Dissolved oxygen, salinity, and temperature were found to be normally distributed. Nutrient data were normalized through log transformation. Log transformed data were checked for potential outliers using the Studentized Residual test. Single data values were removed from general statistical analyses if 1) the value was extremely high and statistically indicated as being an outlier or if 2) inspection of analytical output indicated an analytical problem (i.e. no discernible peak signal).

All data were sorted according to station, tide, month, region, and season. For each of these categories, the means and standard errors were generated. The GLM (General Linear Model) procedure was used to model temperature, salinity, dissolved oxygen and log nutrient concentrations as a function of station, tide, and month, and associated interaction terms for the entire study period. P-values less than an alpha level of .05 indicated statistical significance.

For regional comparisons, the models that were run 1) considered data averaged over both tides and all 15 sampling months and 2) examined seasons separately, but averaged over high and low tide. Three regional comparisons were created for each model. Regional contrasts were statistically significant for p-values less than an alpha level of  $.05/3 = .017$ . For seasonal contrasts, the models that were run 1) averaged data over all eight stations at high and low tide and 2) examined regions separately, but averaged over tides and seasons. Six seasonal comparisons were made for each model. Seasonal contrasts were statistically significant for p-values less than an alpha level of  $.05/6 = .008$ . The Pearson correlation procedure was applied to nutrient, water quality, and flow data to estimate the association between these factors. P-values less than an alpha level of .05 indicated statistically significant correlations. Tables of p-values, from the general linear model, regional and seasonal contrast analyses, and correlations are listed in appendix A. All figures are found in appendix B.



## Results

### Temperature

In the Goose Creek estuary water temperature varied widely from 8 to 31°C. There were significant differences in mean water temperature between high and low tide and among some of the months (Appendix A, Table 2). Monthly mean water temperatures ranged from 9.6 °C in February 1993 to 30.7 °C in July 1993 (Appendix B, Fig. 2). There were no significant differences in temperature between any two regions for the 15 month sampling period and/or within a given season (Appendix A, Table 3). During the study period, the mean water temperature across all eight stations at high tide was significantly higher ( $24.1 \pm 0.1$  °C) than that at low tide ( $23.4 \pm 0.1$  °C). Across the estuarine gradient and within each region, there was no significant difference in water temperature between the fall and spring seasons, but there were significant differences in mean water temperature between all other seasons (Appendix A, Table 4). The largest seasonal difference in mean water temperature occurred between the summer and winter seasons. Seasonal mean water temperatures and their standard errors are listed in Table 24.

### Rainfall

Total rainfall each month for the Goose Creek watershed varied considerably throughout the study period ranging from 1.51 to 10.79 inches (Appendix B, Fig. 3a). Because only 1993 discharge data were available for the reservoir, the rainfall distribution in 1993 will be the focus of discussion. Total monthly rainfalls were highest in the winter and spring. In late spring and throughout the summer, total monthly rainfalls for the watershed were clearly below those averaged over the last 30 years. Specifically, cumulative rainfall for June and July 1993 was more than 5 inches below normal, constituting a moderate drought for the area (S.C. Climatology Office). During the fall, total monthly rainfalls falling on the watershed had decreased, but were comparable to the average total monthly rainfalls in a 30 year period.

### Freshwater Flow

Besides direct rainfall, freshwater entered the Goose Creek estuary from other sources: the Goose Creek reservoir, the Hanahan Wastewater Treatment plant, and the Charleston County Public Waterworks facility. Tributary drainages (urban and forested) also contributed freshwater but their flows weren't measured in this study. Due to the lack of flow data for the Goose Creek reservoir (the largest contributor of freshwater) for the period June to October 1992, results were based on discharge data for the period January to November 1993. Monthly mean freshwater flows from the reservoir and municipal and industrial facilities combined, to the estuary ranged from 4 to 170 cfs, with an estimated mean ( $n=11$ ) of 48 cfs.

The flow of the reservoir discharge was directly related to precipitation. This flow was relatively high during the winter and early spring following peak rainfall in January (Appendix B, Fig. 3a, b). The flow of discharge from the reservoir during this time (January - April) accounted for 96 % of the total freshwater flow to the Goose Creek estuary. During this same time period, flow from both the Charleston County Public Waterworks facility and Hanahan Wastewater Treatment plant represented 2 % of the total freshwater input, respectively. A moderate drought from May to June resulted in no discharge from the reservoir (and subsequently zero flow). At this time, the flow of discharge from Charleston County Public Waterworks facility, the second largest source of freshwater to the Goose Creek estuary, and the Hanahan Wastewater Treatment Plant accounted for 63 % and 37 % of the total freshwater flow to the estuary, respectively (Appendix B, Fig. 3c, d). Monthly mean flows from all three sources during the late summer and fall totaled to < 13 cfs, due generally to dry conditions and low output from the reservoir.

Comparisons of the correlations between salinity in the Goose Creek estuary and the observed average freshwater flow from the Goose Creek reservoir on the day of sampling and two and seven days prior to the day of sampling, respectively, indicated that salinity was most correlated with the average seven day flow. A similar observation has been documented in Cooper River (Sicherman 1989).

In 1993, the average seven day flow (D7Flow) for the reservoir ranged from 0 to 183 cfs (Appendix A, Table 1). In general, the D7Flows for both the Charleston County Public Waterworks

facility and the Hanahan Wastewater Treatment plant were up to 2 orders of magnitude lower than that observed for the reservoir and ranged from 1 to 3 cfs to 1 to 5 cfs, respectively. The peak D7Flow for the reservoir (183 cfs) and wastewater treatment plant (3.2 cfs) occurred in April 1993, and the discharge peak (5.5 cfs) for the Charleston County Public Waterworks facility occurred in August when they were flushing and draining the settling ponds.

### Salinity

Salinity varied from zero to 15 ppt with an overall mean of  $4.6 \pm 0.3$  ppt for the study period. In the estuary, there were significant differences in salinity among stations, between tides, and among months (Appendix A, Table 5). Salinity decreased from the mouth (station 0) to the headwaters (station 6) (Appendix B, Fig. 5). The overall mean salinity, averaged over high and low tide, at stations 0 and 6 was  $8.2 \pm 0.7$  ppt and  $0.6 \pm 0.1$  ppt, respectively. For the 15 month sampling period and each season, there were significant differences in mean salinity between any two regions (Appendix A, Tables 6 & 25; Appendix B, Fig. 4). Values were significantly higher in the lower region than in either the middle or the upper region over the entire study period and during the summer and fall. The same results were observed between the middle and upper regions, with the former being significantly higher. During the winter, salinity measurements in the lower estuary were significantly higher than those in the middle and upper regions of the estuary.

The overall mean salinity in Goose Creek at high tide ( $5.5 \pm 0.1$  ppt) was significantly higher than at low tide ( $2.9 \pm 0.1$  ppt) (Appendix B, Fig. 4). Salinity in the estuary did not significantly differ between fall and summer seasons, but significant differences between other seasonal comparisons occurred (Appendix A, Table 7). For the lower region, salinity in the fall was significantly higher than that during the winter and spring. The mean salinity for the winter season was lower than that found in the spring and summer in the lower region. The mean concentrations of salinity during the fall and summer were significantly higher than in the winter in the middle region of the estuary. In the upper estuary, the mean concentration in the fall was significantly higher than that during the winter. Seasonal means and their standard errors for salinity in the three regions are shown in Appendix A, Table 25.

Statistics indicated a significant negative correlation (Appendix A, Table 23,  $r = -0.14$ ) between salinity and the rate of freshwater flow to the estuary. High salinity levels during the summer and fall coincided with low average seven day flows from the Goose Creek reservoir. Conversely, low salinity measurements during the winter coincided with average seven day flows from the reservoir that were up to 2 orders of magnitude higher than the low flows in the summer.

### Dissolved Oxygen

Dissolved oxygen concentrations ranged from 2.7 to 9.4 mg/l with a mean of  $5.8 \pm 0.1$  mg/l for the study period. Statistical analysis indicated that there were significant differences in dissolved oxygen between stations, among tides, and between months (Appendix A, Table 8). The overall mean concentrations for main channel stations ranged from  $5.5 \pm 0.2$  mg/l at station 4 to  $6.1 \pm 0.3$  mg/l at stations 5b. The mean dissolved oxygen concentration for any individual station was on average within 0.7 mg/l of the daily average of 5.0 mg/l reported for South Carolina tidal waters. During the summer there were significant differences in dissolved oxygen between the three regions (Appendix A, Table 9). The mean concentration observed in the upper region was significantly lower than that in the middle and lower regions in the Goose Creek estuary (Appendix A, Table 25).

The spatial distribution of dissolved oxygen in the estuary during the summer displayed a midestuarine dissolved oxygen sag downstream from the municipal point source discharge at high tide, and lower dissolved oxygen measurements in the lower region of the estuary at low tide (Appendix B, Fig. 7). This same pattern was observed for the 15 month sampling period (Appendix B, Fig. 8).

Dissolved oxygen within the Goose Creek estuary did show an apparent tidal trend. The 15 month average for dissolved oxygen at low tide ( $5.4 \pm 0.1$  mg/l) was significantly lower than at high tide ( $6.0 \pm 0.1$  mg/l). Concentrations of dissolved oxygen, averaged over all eight stations and tide combined displayed a distinct temporal trend in the Goose Creek estuary (Appendix B, Fig. 6).

Monthly mean dissolved oxygen concentrations were inversely related to monthly mean water temperatures, with the peak mean concentration of 8.9 mg/l occurring in February 1993 when temperature was 9.6 oC. Conversely, the minimum monthly mean concentration of 3.8 mg/l was found in July 1993 and coincided with the maximum monthly mean water temperature of 30.7 oC. In the estuary, the mean dissolved oxygen concentration in the summer was significantly lower than that observed during the fall, winter and spring seasons (Appendix A, Table 10 ; Appendix B, Fig. 7). The average dissolved oxygen level in the fall was significantly lower than the average values during the winter and spring. During the winter season, the average dissolved oxygen level was significantly higher than that observed during the spring.

In the lower region, the mean dissolved oxygen concentration in the summer was significantly lower than that during the fall, winter, and spring. Additionally, the mean concentration of dissolved oxygen during the winter was higher than that in the fall and spring. Mean dissolved oxygen concentration during the summer was lower than that during the fall, winter, and spring in the middle estuary. And, the concentration during the fall was lower than that during the winter and spring. In the upper region, mean dissolved oxygen concentrations were significantly lower during the fall and summer than during the winter and spring seasons. Overall and seasonal means and their standard errors for dissolved oxygen are reported in Appendix A, Table 26.

For temperature and dissolved oxygen data, there was a significant and strong negative correlation ( $r = -0.702$ ) between these factors for the entire study period (Appendix A, Table 23), suggesting the effects of high solubility and low respiration during the winter; and higher community respiration and lower solubility during the summer.

Dissolved oxygen concentrations measured in waters at the head, from point source discharges, and from urban and forested tributaries over the study period were highly varied. Low levels of dissolved oxygen were observed in waters from urban and forested tributaries. Brown Pond and New Tenant Pond, tributary stations draining forest watersheds, averaged  $4.3 \pm 0.3$  mg/l and  $5.3 \pm 0.5$  mg/l, respectively. Concentrations in urban tidal creeks, Hanahan Creek and Turkey Creek, averaged  $5.8 \pm 0.5$  mg/l and  $6.2 \pm 0.4$  mg/l, respectively. Both the Goose Creek reservoir ( $8.4 \pm 0.7$  mg/l) and Charleston County Public Waterworks facility ( $8.4 \pm 0.6$  mg/l) had the highest levels of dissolved oxygen among all tributary stations to the estuary. The average dissolved oxygen level reported for the Hanahan Wastewater Treatment plant was  $6.6 \pm 0.4$  mg/l.

## Nutrients

### Orthophosphate

Orthophosphate varied between 0.3 and 5.3 ug-at/l with an overall mean of  $1.3 \pm 0.1$  ug-at/l. There were significant differences in orthophosphate concentrations between stations and among sampling months (Appendix A, Table 11). There was a significant difference in the mean orthophosphate concentration between the upper and lower regions during the summer (Appendix A, Tables 12 & 26; Appendix B, Fig. 10). The mean orthophosphate concentration in the upper region was significantly lower than that in the lower region. While there were significant differences in orthophosphate concentrations between some months, there was no clear seasonal pattern (Appendix A, Table 11; Appendix B, Fig. 9).

Figure 11 (Appendix B) shows the overall mean orthophosphate concentrations in waters at the head, in point source discharges, and from urban and forested tributaries. There were significant differences in the overall mean orthophosphate concentration between these external inputs. The overall mean orthophosphate concentration in the wastewater discharge from the Hanahan Wastewater Treatment plant ( $160.2 \pm 62.6$  ug-at/l) was significantly higher than that measured in the waters at all other external stations. Concentrations in waters from forested tributaries ( $1.4 \pm 0.2$  to  $1.8 \pm 1.0$  ug-at/l) were not significantly different from those in waters from urban ( $1.2 \pm 0.2$  to  $1.9 \pm 0.2$  ug-at/l) tributaries. The overall mean orthophosphate concentration in water from the reservoir was  $2.4 \pm 0.6$  ug-at/l.

Although orthophosphate was weakly correlated with ammonium, nitrate, temperature, salinity, and dissolved oxygen as indicated by  $r$  values less than .20 for the entire study period, the associations between temperature and dissolved oxygen and this nutrient were significant (Appendix A, Table 23).

#### Ammonium

Concentrations of ammonium in Goose Creek ranged from 0.1 to 138 ug-at/l with a mean of  $9.7 \pm 1.0$  ug-at/l. Significant differences were not found in ammonium concentration when station, tide, month, and the associated interaction terms were analyzed (Appendix A, Table 15). The spatial pattern for ammonium concentration (Appendix B, Fig. 13) showed high variability at each of the stations along the estuary during the spring, summer, and fall seasons. Therefore, the statistics did not indicate significant regional differences in ammonium within in any season (Appendix A, Table 16). The peak concentration occurred at the station 5b, adjacent to the outfall of the Hanahan Wastewater Treatment plant during the summer. The average ammonium concentration in the municipal wastewater during the summer was  $207 \pm 121.1$  ug-at/l. At this time, concentrations were also elevated in waters from tributaries draining forested and urban watersheds, but streamflow in these tributaries were probably at their lowest monthly value due to dry conditions.

Although a seasonal pattern was not apparent, peak monthly mean ammonium concentrations were observed during the late summer (July 41.5 ug-at/l and August 52.8 ug-at/l), 1993 (Appendix B, Fig. 12). Furthermore, in the estuary, seasonal means for ammonium were similar (Appendix A, Tables 17 & 24).

Over the entire study period, correlations between nitrate and ammonium concentrations and between orthophosphate and ammonium concentrations in Goose Creek were weak and insignificant at the alpha level of .05 (Appendix A, Table 23). There was a strong and significant correlation between ammonium and the average seven day flow for discharge from the Charleston County Public Waterworks facility ( $r = .60$ ).

Figure 14 (Appendix B) depicts the 15 month average ammonium concentrations in waters at different input sites adjacent to the estuary. The overall mean concentration in urban runoff measured in the non-tidal South Turkey Creek ( $24.3 \pm 3.8$  ug-at/l) was significantly higher than that in waters from forested ( $6.5 \pm 2.6$  to  $14.4 \pm 6.1$  ug-at/l) tributaries and in water from the Goose Creek reservoir ( $5.8 \pm 1.6$  ug-at/l). Ammonium concentrations in waters from the tidal urban tributaries, Hanahan ( $18.8 \pm 3.9$  ug-at/l) and Turkey ( $18.5 \pm 2.5$  ug-at/l) Creek, were significantly higher than those in waters from forested tributaries and Goose Creek reservoir. Amongst all external nutrient inputs, the ammonium concentration in the wastewater from the Hanahan Wastewater Treatment plant ( $202.3 \pm 66.4$  ug-at/l) was significantly higher.

#### Nitrate

Nitrate concentrations ranged from 1.0 to 49.5 ug-at/l with a mean average of  $11.9 \pm 0.5$  ug-at/l. There were significant differences in nitrate concentrations between stations (Appendix A, Table 19). The overall mean concentrations for stations in the estuary ranged from  $15.0 \pm 1.7$  ug-at/l at station 5b to  $9.5 \pm 1.0$  ug-at/l at station 2. During the summer, the mean nitrate concentration in the lower region was significantly lower than that in the middle and upper regions of the estuary (Appendix A, Table 20; Appendix B, Fig. 17). Seasonal means and their standard errors for nitrate, by region, are reported in Appendix A, Table 26. The upper part of the estuary received large inputs of nitrified wastewater from the Hanahan Wastewater Treatment plant (nitrate concentrations ranged from 347-1583 ug-at/l) during the summer. Furthermore, the spatial distribution of nitrate in the estuary showed a clear displacement of the peak nitrate concentration in the upper estuary at high tide downstream to the lower estuary at low tide, (Appendix B, Fig. 17).

Monthly mean nitrate concentrations exhibited a distinct seasonal pattern. There were significant month to month variations in mean nitrate concentration in the Goose Creek estuary (Appendix A, Table 19). In estuary, concentrations were highest in the summer and fall and low during the winter, but the mean nitrate concentration during the fall was significantly different from that in the winter (Appendix A, Tables 21 & 24; Appendix B, Fig. 15). Also, significant seasonal

differences were found within the lower region of the estuary. The mean concentration in the lower estuary during the fall was significantly lower than that observed in the winter and spring (Appendix A, Table 21).

When examining overall correlations with nitrate (Appendix A, Table 23), it was found that nitrate was negatively and positively, but weakly correlated with dissolved oxygen ( $r = -.140$ ) and temperature ( $r = .222$ ), respectively. Both correlations, however, were significant. A significant negative correlation between the average seven day flow from the Goose Creek reservoir and the nitrate concentration in the estuary was observed.

The overall mean nitrate concentration in the municipal point source discharge ( $569.7 + 110.0$  ug-at/l) was significantly higher than what was observed in the waters from the reservoir ( $1.5 + 0.4$  ug-at/l) and from forested ( $1.1 + 0.3$  to  $2.9 + 0.9$  ug-at/l) and tidal urban ( $15.2 + 2.1$  to  $25.6 + 3.5$  ug-at/l) tributaries. The 15 month mean nitrate concentrations in waters from urban tributaries were significantly higher than those in waters from forested tributaries and at the head of the estuary (Appendix B, Fig. 18). The overall mean concentration in non-tidal water from the South Turkey Creek was  $42.2 + 8.9$  ug-at/l, but did not significantly differ from that in waters from the tidal urban creeks (Hanahan Creek and Turkey Creek).

#### Urban Stormwater Runoff

Under baseflow conditions (27 July - 2 August), daily streamflows were less than .5 cfs and stream nutrient concentrations in orthophosphate, ammonium, and nitrate ranged from 0.71 - 1.4 ugat/l, 6.3 - 22.7 ugat/l, and 14.4 - 67.6 ugat/l, respectively (Figures 19 a, b, c, and d).

During the rain event, the peak streamflow of 39.8 cfs occurred at 21:20. The peak concentration for orthophosphate (5.6 ugat/l) occurred at a streamflow of 24.5 cfs about 30 minutes behind the peak flow (Fig. 19 b). Ammonium was highly varied during the rain event (Fig. 19 c). Initial dilution of ammonium by 99 % at peak flow and a delayed peak concentration of 99.9 ugat/l .5 hrs after the peak flow was observed. Nitrate, on the otherhand, was distributed in a similar way prior to and during the rain event (Fig. 19 d). However, nitrate concentrations in the stream were the greatest among all three nutrients, varying from 41.2 - 67.2 ugat/l. The peak nitrate concentration occurred also .5 hrs after peak flow.

#### Nitrogen fractions

Concentrations of nitrogen fractions in water samples collected at the eight main channel stations at both high and low tides, on February 2 1993, and their percentages of total nitrogen are shown in Table 27 (Appendix A). Nitrogen fractions included particulate and dissolved organic nitrogen and dissolved inorganic forms such as, ammonium and nitrate. Total nitrogen concentrations were constant at the stations along the estuary with levels ranging from 38.8 - 47.8 ug-at/l. Organic nitrogen dominated in the estuary, comprising 32 to 63 % of total nitrogen in the estuary. In contrast, concentrations of particulate nitrogen were the lowest compared to the other nitrogen fractions, comprising 3.9 (1.5 ug-at/l) to 18.8 (8.6 ug-at/l) % of total nitrogen. Inorganic nitrogen concentrations were intermediate between those for particulate nitrogen and dissolved organic nitrogen, with concentrations accounting for 2.3 (1 ug-at/l) to 40.6 (16.4 ug-at/l) % of total nitrogen. The major form of inorganic nitrogen in the estuary was ammonium (2.3 - 40.6 ug-at/l). Nitrate concentrations were between 3.1 and 10 ug-at/l.

## Summary and Discussion

Water from and in the Goose Creek estuary was analyzed for nutrients (ammonium, nitrate, and orthophosphate) and monitored for physical parameters, (temperature, salinity, and dissolved oxygen), respectively. Water samples were collected monthly, at high and low tides, at eight stations in the estuary from June 1992 to November 1993. During the same sampling period, eight stations adjacent to the estuary which reflected different landuse types were sampled at low tide. Spatial and temporal distributions of the means for nutrients were examined to determine the relative roles of non-point source inputs from urbanized and forested watersheds and point source inputs such as, municipal and industrial in affecting nutrient distributions in the estuary. The influence of these sources will be discussed in the context of seasonal changes in freshwater discharge, watershed runoff and biochemical processes such as, remineralization, adsorption, denitrification, nitrification, and plant uptake. Physical parameters were compared both spatially and temporally, also.

Temperature displayed a distinct seasonal pattern. Significantly higher values of temperature were found in the summer than during the other seasons. Seasonality of temperature values was similar to that for air temperatures. Higher temperatures in high tide water than in low tide water suggest a diurnal effect. These higher temperatures were observed in the afternoon during the regularly scheduled high tide sampling when air temperatures were higher.

The seasonal variability in salinity in the estuary was regulated by freshwater flows associated with Goose Creek reservoir. Statistics indicated a weak but significant negative association between salinity and the rate of freshwater flow. Maximum salinities in the estuary were observed during the summer when freshwater flows from the Goose Creek reservoir were low ( $< 10$  cfs) whereas minimum salinities occurred during the winter when flows to the estuary were high ( $> 75$  cfs).

Salinity in the estuary at high tide compared to that at low tide was higher. The tidal difference was due to the tidal movement of salt water from the Cooper River. At high tide salt water from the Cooper River is transported upstream in Goose Creek, and this water mixes with that in the creek resulting in an increase in the salt content.

Significant spatial variability in salinity was apparent in the Goose Creek estuary. Salinity along the estuary appeared to be regulated by the input of salt water from the Cooper River and freshwater input from the Goose Creek reservoir. Increases in salinity occurred at stations near the mouth of the estuary where the salt water influence of the Cooper River was the greatest. Salinity showed a pronounced dilution at stations in the upper estuary that frequently received freshwater input from the reservoir.

Dissolved oxygen concentrations varied throughout the year and were probably controlled by the seasonal changes in temperature which lead to a seasonal changes in community respiration. Oxygen concentrations were significantly correlated with temperature values ( $r = -.70$ ). Decreases in water temperature apparently favored higher concentrations in the winter in response to a reduction in community respiration. In the estuary, low dissolved oxygen concentrations in the summer suggested an increase in community respiration with increases in water temperature as found in the Chesapeake Bay (Taft et al. 1990 and Welsh and Eller 1991), in the Long Island Sound (Parker and O' Reilly 1991), and for some parts of the Charleston Harbor estuary system (Connelly 1992). Summer oxygen depletion in the estuary occurred when ammonium concentrations in point source discharges were the greatest, so it is possible that ammonium released during the summer can increase the oxygen demand in the estuary.

Waters in the upper region of the estuary were significantly higher in oxygen content than those in either the lower or middle regions. This spatial pattern suggests differences in the rates of respiration and the amounts of organic matter along the estuary. Summer stational means revealed a moderate dissolved oxygen sag in the middle of the estuary downstream from the municipal wastewater treatment plant. Elevated ammonium loading and wetland drainage low in oxygen content probably contributed to this local decline in dissolved oxygen. Although the spatial distribution of based on overall mean dissolved oxygen concentrations for each station revealed a dissolved oxygen depression in the mid-estuarine region, these levels were not sufficiently elevated to pose a threat to aquatic life in the estuary.

Our sampling schedule illustrates the diurnal changes of oxygen as a reflection of the photosynthesis-respiration relationship. Dissolved oxygen concentrations were lower in the morning following increased respiratory demand by the estuarine community at night and higher in the afternoon in response to photosynthetic production of oxygen, regardless of tidal stage.

Orthophosphate displayed a constant seasonal pattern. Throughout the study period concentrations varied from 0.3 to 5.3 ug-at/l with a mean of  $1.3 \pm 0.1$  ug-at/l. These concentrations are comparable to those observed in the Cooper River (Connelly 1992). Adsorption to suspended particles and phytoplankton uptake are major mechanisms controlling orthophosphate in estuarine waters (Day et. al 1989). A net balance between these processes may explain the seasonally unchanging pattern reported in this study. In spite of low orthophosphate concentrations in the estuary throughout the year, the highest concentrations were found in the summer.

During the summer concentrations were higher in the lower region of the estuary than in the upper region, despite elevated orthophosphate (concentration above 800 ug-at/l) loading from the municipal wastewater treatment plant to the upper part of the estuary. Increased levels in the lower estuary were probably due to input from the Cooper River. Significant depletion of orthophosphate in the upper region appears, at least in part, to be the result of increased phytoplankton uptake in response to increased phytoplankton production (chlorophyll a > 40 ug/l, Smith personnel communication). In the Delaware Bay, a chlorophyll a level greater than 50 ug/l resulted in complete depletion of orthophosphate (Lebo and Sharp 1993). The overall mean orthophosphate concentration in municipal wastewater was considerably higher than levels in all other inputs. Orthophosphate levels in the waters from the forested and urban tributaries and in the reservoir were similar.

Ammonium was highly variable. Concentrations ranged from 0.1 to 138 ug-at/l with an overall mean of  $9.7 \pm 1.0$  ug at/l. Although there were no statistically significant differences between the monthly means throughout the year, peak values occurred in late summer and early fall 1993. This seasonal pattern is similar to that reported by Valiela et al. (1978) for a New England salt marsh and by Wolaver et al. (1984) and Whiting et al. (1987) for the North Inlet in South Carolina. Ammonium levels in the estuary appeared, to be in part, regulated by biological process. Increased sediment remineralization of ammonium (Nixon 1981; Whiting et al. 1987; and Seitzinger et al. 1991) and ammonium rich runoff from the marsh surface during low tide exposure (Gardner 1975; Haines 1979; and Imberger et al. 1983) may have contributed to elevated values in low tide at this time. Increases in ammonium levels in the estuary coincided with greater ammonium input from point source inputs and urban nonpoint source runoff even though these inputs made only small contributions to stream flow. The ammonium concentration was as high as 765 ug-at/l in the municipal wastewater and as high as 61 ug-at/l in urban runoff. Throughout the study period, the variability in ammonium along the estuarine gradient was so great that statistical significant spatial differences could not be detected. The overall mean ammonium concentration in municipal wastewater was extremely higher than that in water from the reservoir or waters in urban and forested tributaries. The overall mean ammonium levels in waters from forested watersheds were lower than those in waters from urban watersheds.

Nitrate was the only nutrient studied that displayed a seasonal pattern. Nitrate concentrations in the Goose Creek estuary ranged from 1.0 to 49.5 ug-at/l with an mean of  $11.9 \pm 0.5$  ug-at/l for the study. High nitrate concentrations in the water column in the summer and fall were probably the result of increased nitrification and remineralization, and input from urban nonpoint source discharges. Bernounsky and Nixon (1993) measuring rates of nitrification within the Narragansett Bay found temperature to be the most important factor influencing the annual cycle of pelagic nitrification. These two investigators reported high nitrification rates in the summer, and they feel that the actual rate of this process and the subsequent release of nitrate to the water column depends on the availability of ammonium. Increased regeneration of ammonium from the sediments at higher water temperatures in the summer resulting from senescence and subsequent decomposition of marsh plants in the fall has yielded elevated ammonium concentrations in some estuaries (Valiela et al., 1978; G. J. Whiting et al., 1987). These two investigators reported higher nitrification rates in one of the tributaries to the Narragansett Bay having higher ammonium concentrations. During the summer months, ammonium concentrations in

the wastewater from the Hanahan Wastewater Treatment plant ranged from 347 to 1583 ug-at/l and probably enhanced the nitrification process. There were no measurements made for nitrification in this study, however, concentrations of nitrate maxima in wastewater from the point sources (Charleston County Public Waterworks facility, Hanahan Wastewater Treatment plant) ranged from approximately 15.0 to 1600 ug-at/l over the 1992 to 1993 sampling period. These instantaneous monthly concentrations of nitrate showed great potential for observing increased nitrate concentrations in the water column, particularly at a time of limited watershed runoff. During the warmer months, nitrate concentrations in the wastewater from the Hanahan Treatment plant were 2 to 3 orders of magnitude higher than those measured in the effluent coming from the Charleston County Public Waterworks facility. The urban tributaries (nitrate maxima ranged from 13 to 50 ug-at/l) adjacent to the estuary may have contributed to the high nitrate concentrations during the summer and fall, also. The observed winter decline in nitrate may be explained by denitrification. Denitrification usually occurs in anaerobic environments (e.g. water, sediments) and therefore would be inhibited by an oxidized water column in the winter.

In the summer, nitrate concentrations in the upper region of the estuary were dominated by input from the municipal wastewater treatment plant which elevated levels in this region above those in the middle and lower regions. Appreciable ammonium input from the wastewater treatment plant to the upper estuary may have enhanced nitrification and resulted in elevated nitrate concentrations at this time. Furthermore, the peak nitrate concentration in the upper estuary was transported to the middle of the estuary at low tide and resulted in significantly higher concentrations in the middle of the estuary than in the lower part of the estuary.

Like orthophosphate and ammonium, the overall mean nitrate concentration in municipal wastewater discharge was higher than in waters from the urban and forested tributaries. The overall mean nitrate concentrations in waters from urban tributaries were higher than in waters from forested tributaries. Omernik (1977) found that nitrate levels in streams draining forested watersheds were low in comparison to those in streams draining deforested basins.



## REFERENCES

- American Public Health Association, 1985. Standard methods for the examination of water and wastewater. Washington, DC. 1268p.
- Bernounsky, V. M. and S. W. Nixon, 1993. Rates of nitrification along an estuarine gradient in Narragansett bay. *Estuaries*. 16, 4:718-730.
- Boynton, W. R. and W. M. Kemp, 1985. Nutrient regeneration and oxygen consumption by sediments along the estuarine salinity gradient. *Marine Ecology Progress Series*. 23, 45-55.
- Connelly, K., 1991. Spatial and temporal patterns of nutrient distribution in the Cooper River estuary. Masters Thesis, University of South Carolina Press, Columbia, S.C.
- Corbett, E. S., J. A. Lynch, and W. E. Copper, 1978. Timber harvesting practices and water quality in the eastern United States. *Journal of Forestry*. 76, 8:484-488.
- Correll, D. L., T. E. Jordan, and D. Weller, 1992. Nutrient flux in a landscape: Effects of coastal landuse and terrestrial community mosaic on nutrient transport to coastal waters. *Estuaries*. 15, 4:431-442.
- Davenport, T., 1994. EPA'S perspective - you need to protect water quality. *Journal of Soil and Water Conservation*. 49, 1-93.
- Day, J. W., Jr., C.A.S. Hall, W. M. Kemp, and A. Yanez-Azrancilbia, 1989. *Estuarine ecology*. John Wiley & Sons, New York. 558p.
- Degobbins, D., 1973. On the storage of seawater samples for ammonia determination. *Limnology and Oceanography*. 18, 146-150.
- Fischer, T. R., L. W. Harding, Jr., D. W. Stanley, and L. G. Ward, 1988. Phytoplankton, nutrients, and turbidity in the Chesapeake, Delaware, and Hudson estuaries. *Estuarine, Coastal and Shelf Science*. 27, 61-93.
- Gardner, L. R., 1975. Runoff from an intertidal marsh during tidal exposure-recession curves and chemical characteristics. *Limnology Oceanography*. 20, 81-89.
- Haines, E. B., 1979. Nitrogen pools in Georgia coastal waters. *Estuaries*. 2, 34-39.
- Hopkins, R. B. and J. C. Clausen, 1985. Land use monitoring and assessment for nonpoint source pollution control. *Perspectives on non-point source pollution: proceedings of a national conference, Kansas City, Missouri, Washington, D. C. : U. S. Environmental Protection Agency, Office of Water Regulations of Standards*. 25-39.
- Imberger, J., T. Berman, R. R. Christian, E. B. Sherr, D. E. Whitney, L. R. Pomeroy, R. G. Wiegart and W. J. Wiebe, 1983. The influence of water motion on the distribution and transport of materials in a salt marsh estuary. *Limnology and Oceanography*. 28, 201-214.
- Jaworski, J. A., G. Groffman, A. A. Keller, and J. G. Prague, 1992. A watershed nitrogen and phosphorus balance: The upper Potomac River basin. *Estuaries*. 15 1:83-85.
- Johnes, P. J. and A. L. Heathwaite, 1992. A procedure for simultaneous determination of total nitrogen and total phosphorus in freshwater samples using persulphate microwave digestion. *Water Research*. 26 10:1281-1287.

- Kemp, W. M., P. Sampou, J. Caffrey, M. Mayer, D. Henriksen, and W. R. Boynton, 1990. Ammonium recycling versus denitrification in Chesapeake Bay sediments. *Limnology and Oceanography*, 35, 7:1545-1563.
- Koike, I., and J. Sorensen, 1988. Nitrate reduction and denitrification in marine sediments. In: Blackburn, T. H. and Sorensen, J. (eds). *Nitrogen cycling in coastal marine environments*, John Wiley & Sons, Ltd. New York. 251-272.
- Lebo, M. E., and J. H. Sharp, 1993. Distribution of phosphorus along the Delaware, an urbanized coastal plain estuary. *Estuaries*. 16, 290-301.
- Martin, C. W., D. S. Noel, and C. A. Federer, 1984. Effects of forest clearcutting in New England on stream chemistry. *Journal of Environmental Quality*. 14, 3:204-210.
- McCarty, J. J., W. R. Taylor, and J. L. Taft, 1977. Nitrogenous nutrition of the plankton in the Chesapeake Bay. 1. Nutrient availability and phytoplankton preferences. *Limnology and Oceanography*. 22, 6:996 -1011.
- Murphy, J. and J. P. Riley, 1962. A modified single-solution method for the determination of phosphate in natural waters. *Analytical Chemistry. Acta*. 27, 31-36.
- Nisho, T., I. Koike, and A. Hattori, 1982. Denitrification, nitrate reduction, and oxygen consumption coastal and estuarine sediments. *Applied Environmental Microbiology*. 43, 648-53.
- Nixon, S. W., 1981. Remineralization and nutrient cycling in coastal marine ecosystems, In: Neilson, B.J. and L. E. Cronin (eds.). *Estuaries and Nutrients*. Humana Press, New York. 330 p.
- Omernik, J. M., 1977. Nonpoint source-stream nutrient level relationships: A nationwide survey. EPA-600/3-77-105. *Eco. Res. Ser.* U.S. Environmental Protection Agency, Washington D. C.
- Parker and Reilly, 1991, Oxygen depletion in Long Island Sound: A historical perspective. *Estuaries*. 14, 248-264.
- Pennock, J. R., 1987. Temporal and spatial variability in phytoplankton ammonium and nitrate uptake in the Delaware estuary. *Estuarine, Coastal and Shelf Science*. 24, 841-857.
- Peterson, D. H., R. F. Smith, S. W. Hager, D. D. Harmon, R. E. Herndon, and L. E. Schemel, 1985. Interannual variability in dissolved inorganic nutrients in northern San Francisco Bay estuary. *Hydrobiologia*. 119, 39-58.
- Rao, R., Charleston Harbor Project, Department of Environmental Health Science. University of South Carolina, Columbia, SC. Personal communication.
- Ryther, J. H. and W. M. Dunstan, 1971. Nitrogen, phosphorus, and eutrophication in the coastal marine environment. *Science*. 171, 1008-1013.
- SAS Institute, Inc., 1985 SAS user's guide: statistics, version 5 edition. SAS Institute, Cary, NC, 1290p.
- Seitzinger, S. P., 1982. The importance of denitrification and nitrous oxide production in the nitrogen dynamics and ecology of Narragansett Bay, Rhode Island. Ph. D. Thesis, University of Rhode Island.

Seitzinger, S. P., W. S. Gardner, and A. K. Spratt, 1991. The effect of salinity on ammonium sorption in aquatic sediments: implications for benthic nutrient recycling. *Estuaries*. 14, 2:167-174.

Sicherman, T. L., 1989. Spatial and temporal variation of chlorophyll-a and organic carbon in the Cooper River Estuary, South Carolina. Master's Thesis. University of South Carolina, Columbia, SC.

Smith, A., Charleston Harbor Project, Department of Environmental Health Sciences. University of South Carolina, SC. Personal communication.

Solarzano, L., 1969. Determination of ammonia in natural waters by the phenol hypochlorite method. *Limnology and Oceanography*. 14, 799-801.

South Carolina Climatology Office, Southeast Regional Climatology Center.

Sweeney, B. W., 1992. Streamside forests and the physical, chemical, and trophic characteristics of piedmont streams in eastern North America. *Water Science Technology*. 26, 12:2653-2673.

Taft, J. C., W. Rowland Taylor, E. O. Hartwig, and R. Loftus, 1980. Seasonal oxygen depletion in Chesapeake Bay. *Estuaries*. 3, 242-247.

Teague, K. G., C. J. Madden, and J. W. Day, Jr., 1988. Sediment-water oxygen and nutrient fluxes in a river-dominated estuary. *Estuaries*. 11, 1:1-9.

Virtousek, P. M. and J. M. Meillo, 1979. Nitrate losses from disturbed forests: patterns and mechanisms. *Forestry Science*. 25, 605-619.

Valiela, I. and J. M. Teal, et al., 1978. Nutrient and particulate fluxes in a salt marsh ecosystem: Tidal exchanges and inputs by precipitation and groundwater. *Limnology Oceanography*. 27, 798-812.

Valiela, I. and K. Foreman, et al., 1992. Couplings of watersheds and coastal waters: Sources and consequences of nutrients enrichment in Waquoit Bay, Massachusetts. *Estuaries*. 15, 443-457.

Welsh, B. L. and Eller, 1991. Mechanisms controlling summertime oxygen depletion in western Long Island Sound. *Estuaries*. 14, 251-265.

Whiting, G. J., H. N. McKellar, Jr., B. Kjerfve and J. D. Spurrier, 1987. Nitrogen exchange between a southeastern USA salt marsh ecosystem and the coastal ocean. *Marine Biology*. 95, 173 -182.

Wolaver, T. G., W. Johnson and M. Marozas, 1984. Nitrogen and phosphorus concentrations within North Inlet, South Carolina - speculation as to sources and sinks. *Estuarine, Coastal and Shelf Science*. 19, 243 - 255.